PREPARATION OF GOLD NANOPARTICLES IN POLYSTYRENE - PEO BLOCK COPOLYMERS: THE ROLE OF ULTRASOUND

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(Modifications highlighted in red)

Abstract

This work reports the preparation of ordered arrays of gold nanoparticles by sonochemically enhanced borohydride reduction of precursor lithium tetrachloroaurate ($LiAuCl_4$) incorporated into the core of polymeric micelles formed from amphiphilic copolymers of polystyrene (PS) and poly(ethylene oxide) (PEO). The copolymers were prepared with varying styrene block lengths from a PEO macroinitiator by atom transfer radical polymerization (ATRP). UV/visible spectroscopy was used to confirm the formation of elemental gold and the effect of sonication time on the appearance of the gold nanoparticles was determined and showed that the absorbance first increased as the nanoparticles formed but decreased at longer times, presumably due to a degree of agglomeration. Transmission electron microscopy revealed the morphology of the nanocomposites which confirmed that micellar polystyrene-block-polyethylene oxide is an excellent vehicle for the formation of well-defined films containing nanoparticulate gold. However, we report for the first time that care must be taken to optimise the preparation time to obtain the desired particle sizes since this parameter is very sensitive to the duration over which sonication is carried out.

Keywords: Nanocomposite, block copolymer, ultrasound, gold.

Introduction

Nanometer sized particles of metals and semiconductors have been investigated intensively in recent years because of the influence which their small sizes has on their electronic properties, for example in structures such as quantum wires, quantum wells and quantum dots [1-4]. In order to fabricate such electronic devices, it is necessary to develop methods to produce structured arrays containing nano-sized metal or semiconductor islands separated by non-conductive, tunnel barriers [5] in a periodic structure. Most physical nanofabrication techniques such as electron-beam or scanning probe lithography are costly and time consuming for producing large-scale devices. Many methods of forming composite nanoparticles have been developed based on chemical methods [6]. The general principle of such methods is to combine nano-scale metal or semiconductor particles with processable matrices, such as polymer or copolymer micelles.

Under near-equilibrium conditions, block copolymers can self-organize into a variety of nanometre-sized micro phase-separated structures. The structures formed depend on the relative volume fractions, the Flory-Huggins interaction parameter and the degree of polymerization of each block [7, 8]. Systems containing block copolymers are also of great interest since they form multiphase morphologies with interesting and useful self-assembly or phase separation behavior. They can offer some advantages compared with low molecular weight surfactants with respect to the long-term stability of the self-organized structures as well as the ability to form films [9]. Block copolymers not only form micelles in solution but also can assemble in solid films with a regular micro-domain structure. Furthermore, the critical micelle concentration of block copolymers is typically lower and their kinetic stability is higher than that of low molecular weight surfactants. By selecting an appropriate solvent, an amphiphilic block copolymer can form micelles with a soluble shell and insoluble core capable of binding metal salts or adsorbing at the surface of an inorganic particle. Precursor components can be introduced into the core of the micelles and subsequently converted to nanoparticles. In this way, the micelles act as nano-scale “reaction vessels” where the sizes of the metal or semiconductor nanoparticles can be varied and controlled along with those of the potential barriers that control their separation. With these advantages, block copolymers are intriguing candidates for preparing composite containing nanoparticles that can be applied in nanotechnology and nanofabrication, for example in block copolymer lithography [5]. Block copolymer micelles with cores containing ethylene oxide or vinyl pyridine have also been

used to form and stabilize gold particles from an aqueous solution and to cast films in which the particles are homogeneously dispersed [10, 11].

For this work, in an attempt to prepare nano-structured composite films, we used atom transfer radical polymerization, ATRP, to synthesize amphiphilic diblock copolymers of polystyrene and poly(ethylene oxide), PS-*b*-PEO, with varying styrene block lengths. The copolymers formed micelles in organic solvents with hydrophilic PEO cores inside which gold nanoparticles could be generated by reduction of a gold salt [12, 13]. The self-organization of block copolymers is sensitive to the presence of low molecular weight compounds such as the solvent or the inorganic precursor. Particle and film formation is usually accompanied by complex transformations of the equilibrium structure of the copolymer. In order to avoid this loss in structural control, we chose an approach where the kinetic stability of the micelles formed in dilute solution was sufficient to be retained after removal of the solvent from cast films. [14-16]. However, while applying the sonochemical reduction method employed by Moller and co-workers, a strong dependence of the resulting gold nanoparticle size on sonication conditions was noted so that this work also investigates this for the first time with an aim to controlling and optimizing the reaction.

Experimental

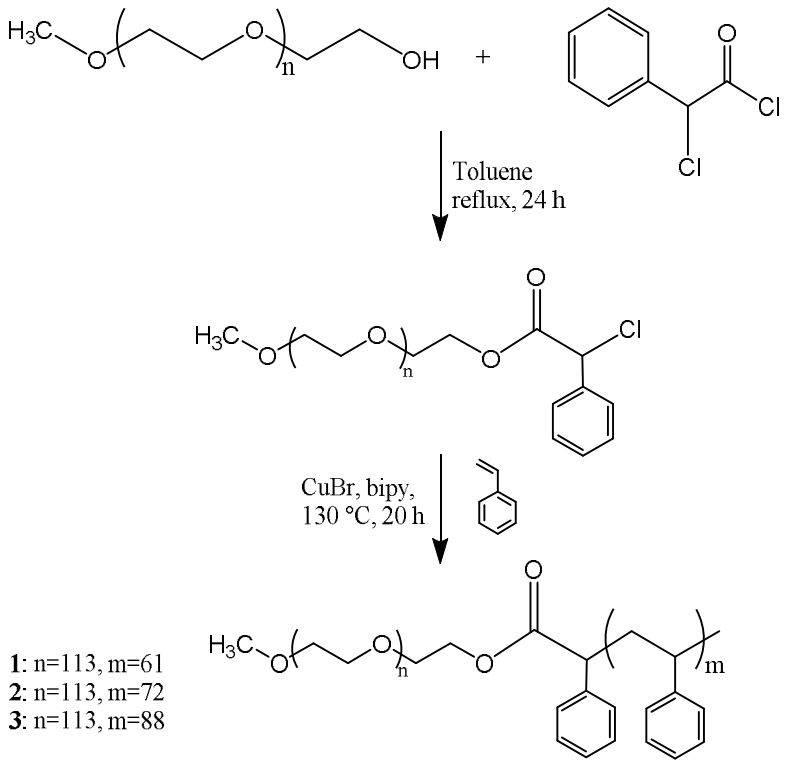
Materials

α-Chlorophenylacetylchloride (Aldrich) was distilled over a Vigreux column and used as received. Poly(ethylene oxide) monomethyl ether (MePEO) 5000 (Aldrich) was dried by removing residual water by azeotropic distillation with toluene on a water separator. Inhibitors in styrene were removed by passing the monomers through an aluminium oxide column. CuBr (98%, Aldrich) and 2,2-bipyridine (bipy) and poly(vinyl pyrollidone) (PVP) (all Aldrich) were used as received. Polymerization was carried out in an inert gas atmosphere using nitrogen (Linde) gas which was passed over molecular sieves (4Å) and finely distributed potassium on aluminium oxide (Aldrich). $LiAuC1_4$ and $NaBH_4$ used for the generation of gold nanoparticles were also from Aldrich.

Preparation and characterization of PEO copolymers with styrene

Preparation of the macroinitiator of PEO and its copolymerization with styrene, summarized in Scheme 1, has previously been described in detail [17]. Three block copolymers (**1** – **3**) with fixed PEO block length and varying amounts of styrene were prepared. The macroinitiator and block copolymers were characterized by ^{1}H NMR, using Bruker Avance

250 and 300 MHz spectrometers using $CDCl_3$ as solvent. The block copolymer composition was determined by the ratio of the NMR signals intensity of the phenyl peak region to that of the alkyl PEO region. The number average, M_n, and weight average, M_w, molecular weights were determined using a Varian PL-GPC 50 Plus gel permeation chromatograph with THF at a flow rate of 1 ml/min through a Polymer Laboratories PLGel 5 μm 'mixed' columns calibrated with polystyrene standards.



Scheme 1

Synthesis of Gold Nanoparticles

Solutions of 1% (w/w) (PS-*b*-PEO) copolymers were prepared in toluene to form micelles. $LiAuC1_4$ (0.1 or 0.2 equivalents of $LiAuC1_4$ bound per ethylene oxide) was added and sonicated using a cleaning bath (30 kHz, delivering 0.4 W of power into the reaction) for 1 h to obtain a bright yellow solution. Solid sodium borohydride ($NaBH_4$, ca. 0.05 g) was then added and sonication continued for a further 1 h during which the solution gradually became a deep purple colour. In parallel experiments for comparison, gold nanoparticles were prepared using the same method replacing the block copolymer with poly(vinyl pyrollidone), PVP. The formation of elemental gold was confirmed by UV/Vis absorption spectroscopy

using an Agilent 8453 UV-Visible Spectrophotometer with a 1.0 cm path length quartz cuvette, monitoring the presence of a peak around 520 nm.

Transmission Electron Microscopy (TEM)

One drop of a diluted purple solution with a block copolymer concentration of 0.1% in toluene was placed on a carbon-coated copper grid and the solvent allowed to evaporate. TEM micrographs (JEOL JEM 1200, 80 kV) were recorded. In order to minimize charging and damage to the polymer, the electron beam intensity was kept as low as possible.

Results and Discussion

Atom transfer radical polymerization (ATRP) has been developed into a versatile example of controlled radical polymerization [18] based on a rapid and reversible exchange between a low concentration of growing radicals and dormant species mediated by redox processes at copper. A hydroxyl-terminated PEO polymer was modified to form an ATRP macroinitiator which was reacted with varying amount of styrene to give copolymers **1** – **3** with structures PS_{61}-*b*-PEO_{113}, PS_{72}-*b*-PEO_{113} and PS_{88}-*b*-PEO_{113}. As expected for a living reaction, low polydispersities (M_w/M_n) were obtained as shown in Table 1 which also shows the number average molecular weights (M_n) of each of the materials. GPC chromatograms were symmetrical and showed the chain extension due to addition of styrene (Figure 1).

Table 1. GPC data for the block copolymer samples

Polymer	Composition*	M_w	M_n	M_w/M_n
3	PS_{88}-b-PEO_{113}	15630	14370	1.09
2	PS_{72}-b-PEO_{113}	15240	13830	1.10
1	PS_{61}-b-PEO_{113}	11950	11260	1.06

* Determined by ^{1}H NMR

The formation of elemental gold was confirmed by the UV/Vis absorption spectra showing the typical plasmon resonance around 520 nm [19]. Figure 2 shows a typical series of absorption spectra recorded during the borohydride reduction reaction. The spectra for the gold nanoparticles in the three block copolymer samples (PS-*b*-PEO) and PVP each showed an absorption maximum in the range of 519 nm to 525 nm depending upon the particle size

(Figures 3 - 6). A lower absorption maximum wavelength is associated with a smaller average size of the Au particles [20].

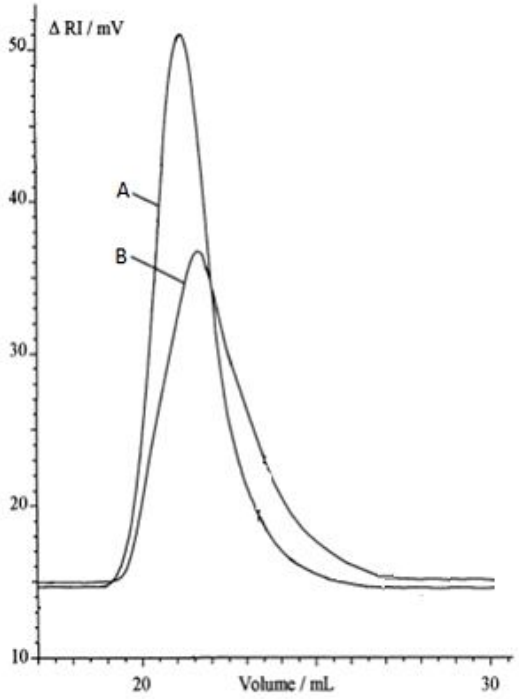


Figure 1. GPC chromatograms of (A) PS_{61}-b-PEO_{113} block copolymer and (B) PEO-macroinitiator showing the chain extension

It has been established that two major factors which control the size and arrangement of the nanoparticles are the stability of the copolymer micelles in the media and the strength of the interactions between the PEO block and the gold nanoparticles [21]. In this case, the interactions are relatively weak so that the micelles are not affected by the process of particle formation and, in turn, do not influence particle growth to any great extent, for example by adsorption of the polar block onto the growing nano-crystallites. By comparison, the interactions between PVP and Au are rather strong [22] and it has been reported that a high density of small Au crystals distributed in PVP did not agglomerate because of the formation of polymer bridges between crystallites. The bridging effect can be potentially be eliminated by adding a third component [23].

Also of great interest is the previously unreported time dependence of the UV spectra. Figure 2 shows that the absorbance increases as the reduction reaction proceeds due to the formation of higher concentrations of nanoparticles. Significantly, the wavelength of maximum absorption does not change, indicating only a small variation, if any, in average particle size. However, of potentially greater interest is that further changes occur after

sonication is stopped. Figures 3 - 6 show that the absorbance continues to grow for around 10 min (except in the case of **3**, the longest polystyrene block) even when the reaction vessel is removed from the ultrasound bath but then falls markedly. We ascribe this to agglomeration [24] of the small nanoparticles into larger clusters. In the case of **3**, the absorbance simply decreased with the sonication time which may be due to its high PS molecular weight keeping the PEO and NPs further separated or disintegration of bridged micelles and aggregated particles.

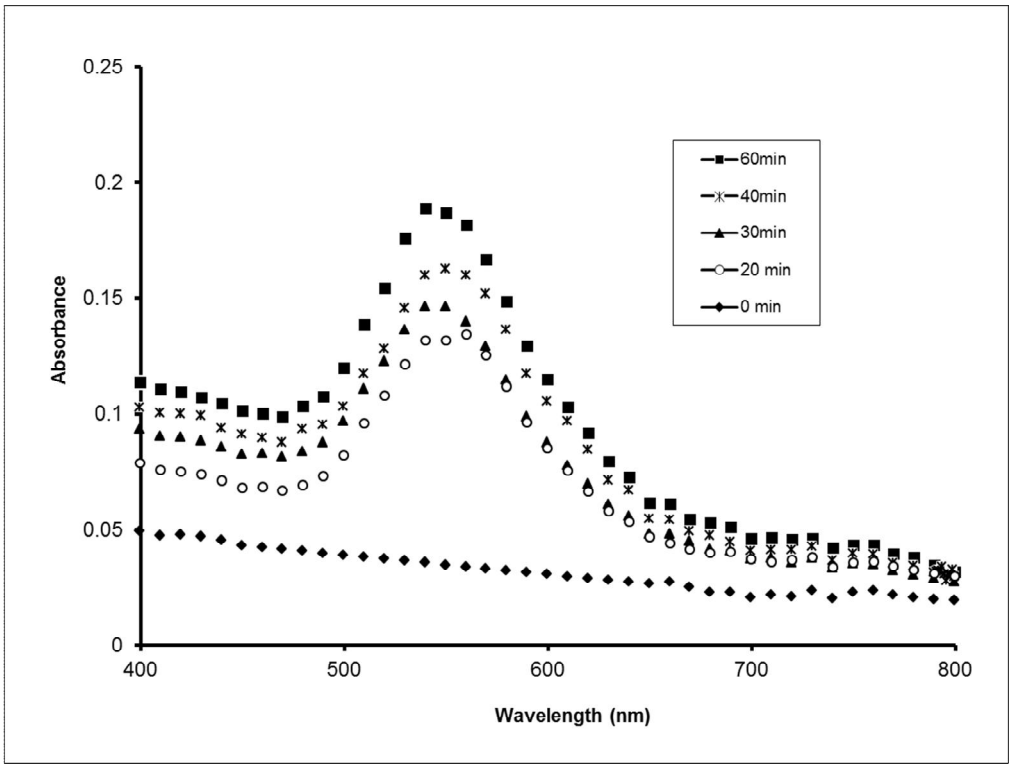


Figure 2. Absorbance spectra for gold nanoparticles in PS-b-PEO during sonochemical borohydride reduction

The morphology and phase separation of cast films of the block copolymers **1** – **3**, determined by scanning electron microscopy, has been shown previously. The composite nanoparticles formed a hexagonal array [17]. Transmission EM images of the Au/PS-*b*-PEO composites and Au/PEO nanoparticles are illustrated in Figures 7 and 8, respectively. The dark spots represent the micelle cores with individual or clusters of gold nanoparticles. The individual nanoparticles range between 8 – 18 nm in size and are predominantly spherical although there are a few that have distorted shapes. This indicates that the gold was well

dispersed in the micelles. The brighter areas between the dark spots represent the shell of the micelles which separate the gold nanoparticles. The size of the gold particles corresponded to the plasmon resonance [25]. Some agglomeration was also noted as in Figure 7(c). Comparison of the images for the block copolymers with those using only PEO (M_n = 5000) confirms the nanoparticles were formed inside the micellar cores although considerably more agglomeration was noted here due to the absence of the PS block to separate the micelle interiors.

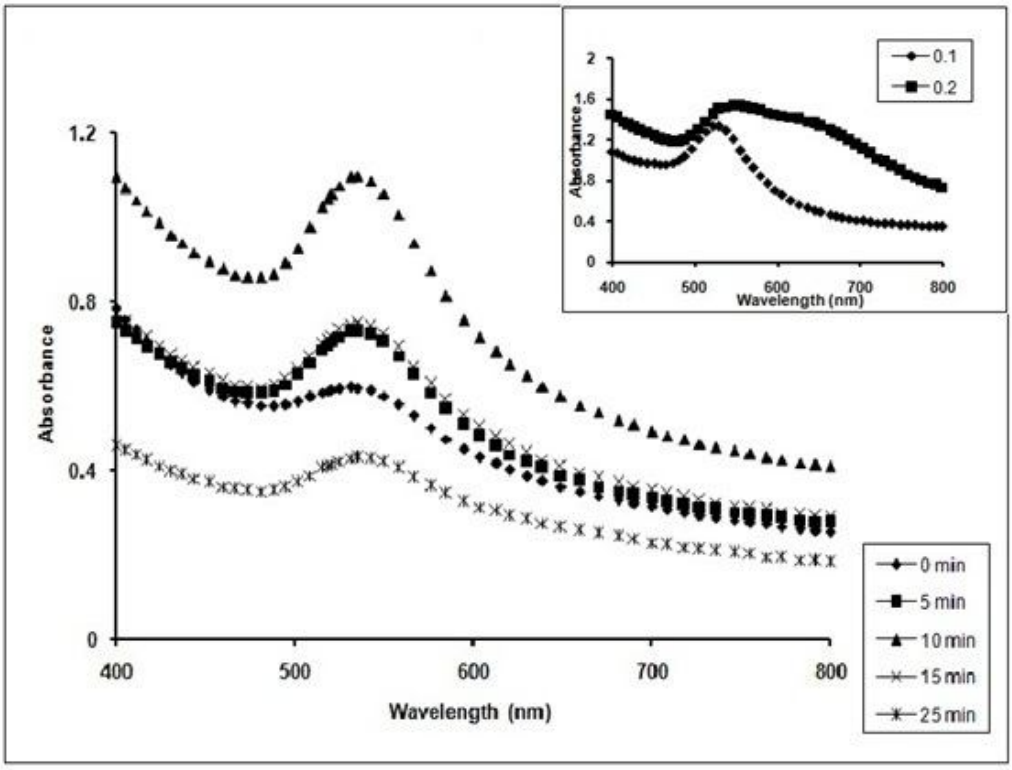


Figure 3. Absorbance spectra for gold nanoparticles in (1) at different times after sonication; the inset shows the absorbance just after the formation of nanoparticles at two different loading ratios of gold:ethylene oxide.

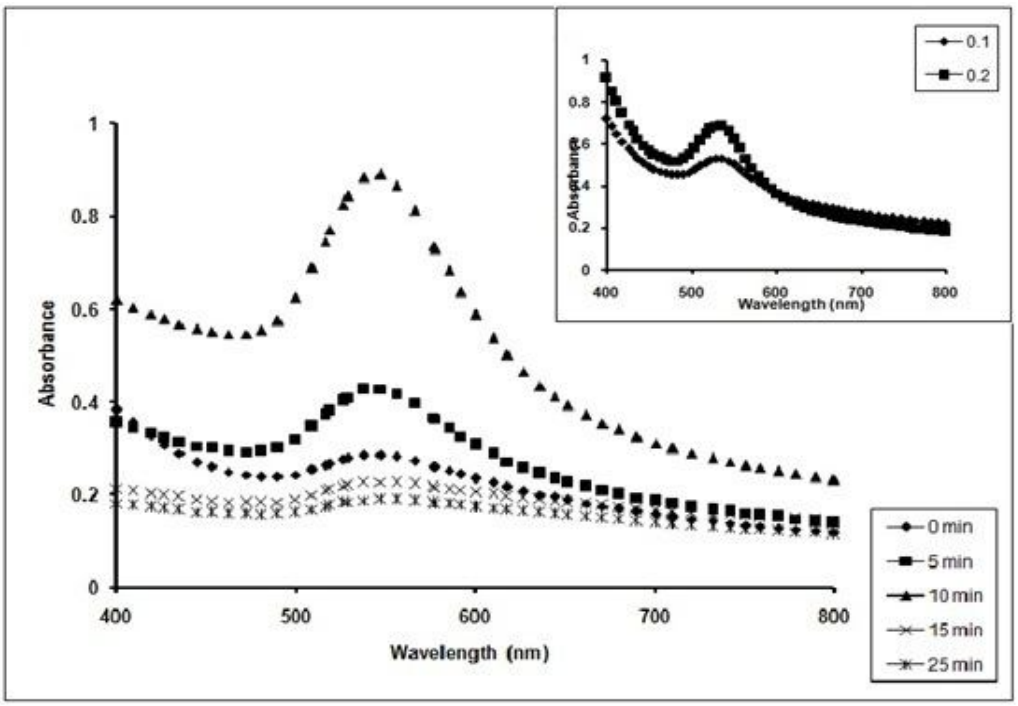


Figure 4. Absorbance spectra for gold nanoparticles in (2) at different times after sonication; the inset shows the absorbance just after the formation of nanoparticles at two different loading ratios of gold:ethylene oxide.

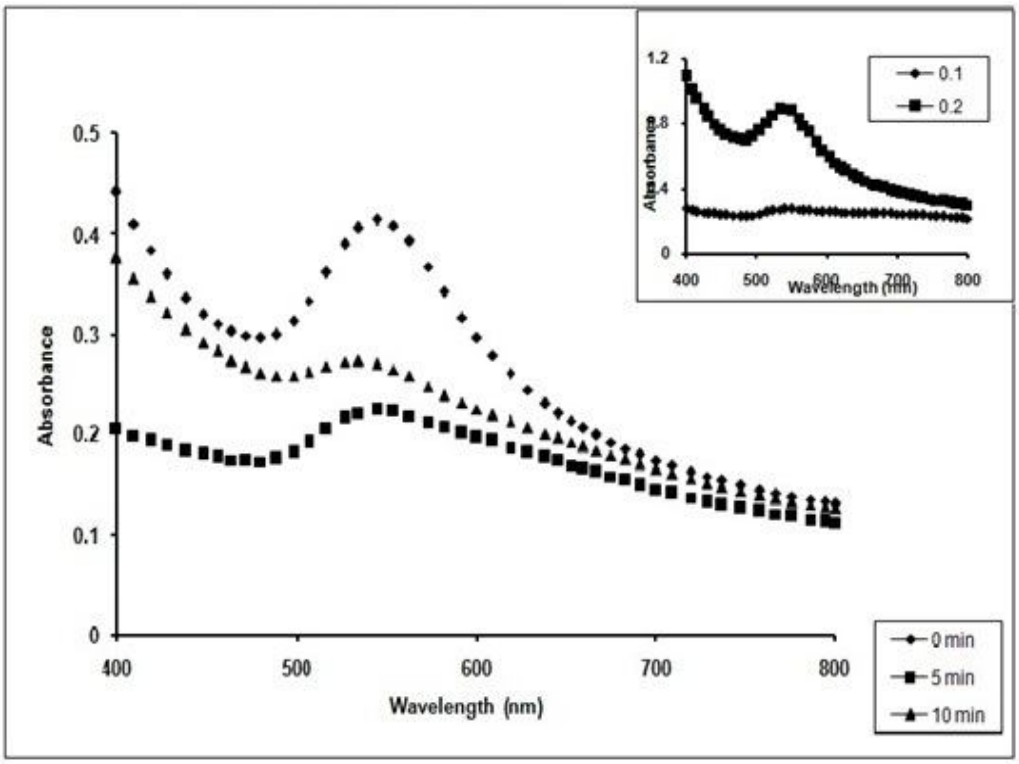


Figure 5. Absorbance spectra for gold nanoparticles in (3) at different times after sonication; the inset shows the absorbance just after the formation of nanoparticles at two different loading ratios of gold:ethylene oxide.

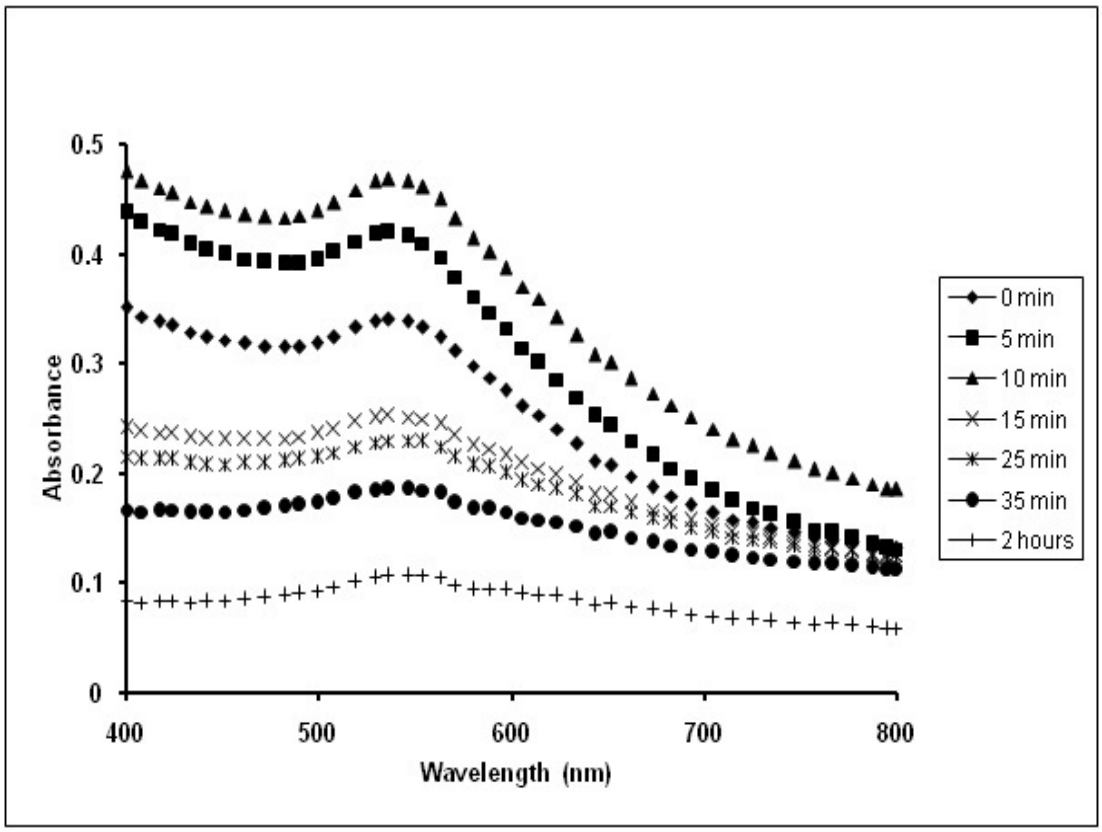


Figure 6. Absorbance spectra for gold nanoparticles in PVP at different times after sonication;

Additional insight into the changes that occurred during the transformation process was also obtained by TEM. It has been shown that amphiphilic diblock copolymer micelles in a non-polar solvent can exhibit high kinetic stability and that films consisting of densely packed micelles can be prepared by evaporation of the solvent. The spherical agglomerates of dark spots marked the micelles and represented the clusters of elemental gold suggested by the UV spectra arising from a degree of agglomeration of the individual nanoparticles. Taking into account the strong contrast between the core and shell of the micelles as well as the evidence of the UV/visible spectra we conclude that the Au is dispersed as small clusters of elementary gold within the cores of the micelles. It is known that Au nanoparticles exhibit a weak, broad absorbance band below 500 nm. Thus, the reduction of the typical plasmon resonance of small Au particles around 520 nm can be explained by the agglomeration at longer reaction times.

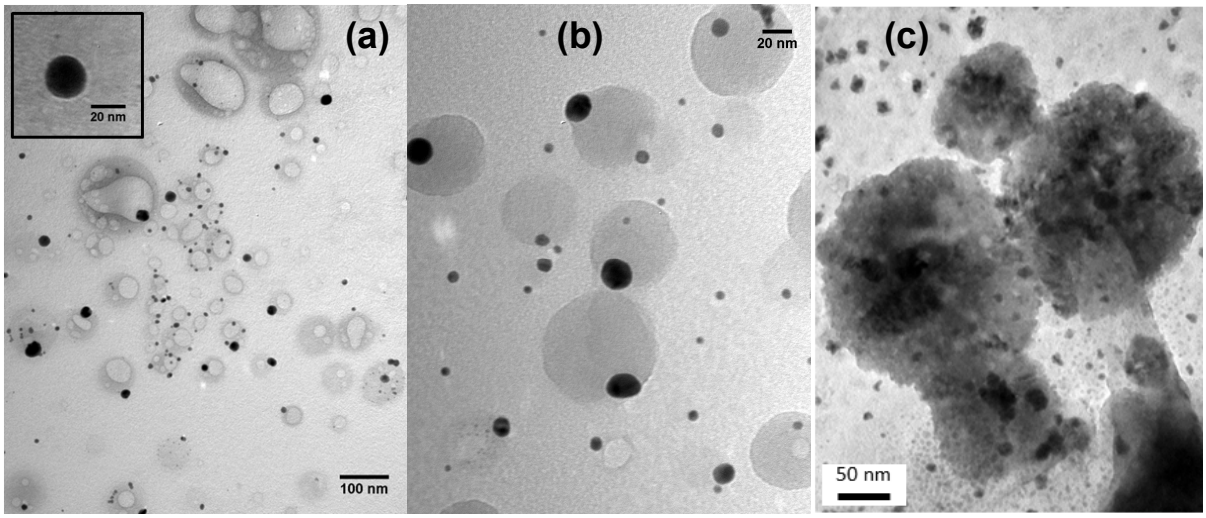


Figure 7. TEM image for Au nanoparticles in (a) copolymer (1); (b) copolymer 2; (c) copolymer (3).

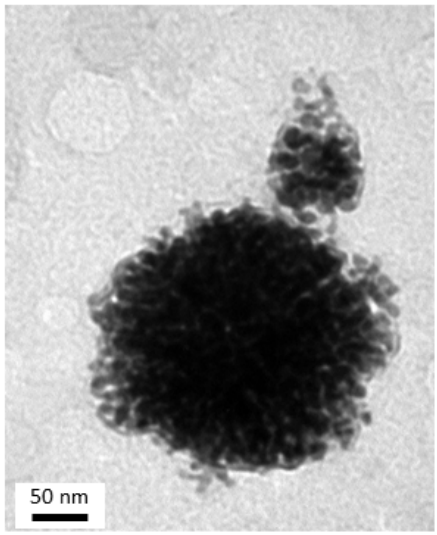


Figure 8. TEM image for Au nanoparticles PEO.

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We conclude that polystyrene-*b*-PEO micelles provide an excellent means for the formation of well-defined films containing nanoparticulate gold, the size of which can be controlled by variation of the loading ratio and the micelle size as well as the reaction time [15]. However, care must be taken to select the optimum reaction and processing time to achieve a balance between the individual nanoparticles and clusters. In particular, the sonication time must be optimised as prolonged reaction times lead to significant agglomeration with deterioration in optical performance. Kinetic control of the block copolymer structure was found to be very effective in arranging the nanoparticles coherently.

Other nanoparticles, of for example platinum, palladium, TiO_2, Ag or semiconductors, can be incorporated into micellar films using the described approach.

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